

PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Improvements in or relating to Dehydrogenation Catalysts

(A communication from STANDARD OIL DEVELOPMENT COMPANY, a Corporation duly organised and existing under the Laws of the State of Delaware, United States of America, having an office at Linden, New Jersey, United States of America).

I, JOHN CONRAD ARNOLD, a British Subject of 29, Southampton Buildings, Chancery Lane, London, W.C.2, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

The present invention relates to improved dehydrogenation catalysts of particular use in the conversion of secondary alcohols to ketones.

It is well known that the dehydrogenation of secondary alcohols to the corresponding ketones may be achieved by passing the alcohols at elevated temperatures over substances acting as dehydrogenation catalysts. In the early stages of development in this field, metals such as copper, brass, etc. were employed in this type of reaction. These catalysts possess the disadvantages of high operating temperatures and short life. Somewhat later, difficulty reducible oxides such as zinc oxide, cerium oxide, magnesium oxide, etc., attained considerable prominence as dehydrogenation catalysts. Various combinations of catalytic metals and difficulty reducible oxides have also been employed from time to time. It was found that difficulty reducible oxides have a dehydrating as well as a dehydrogenating effect and that due to the dehydrating effect, considerable olefin was regenerated from the alcohol which reduced the overall yield of ketone. In an attempt to minimize these side reactions, additives such as the alkali or alkaline earth metal carbonates or hydroxides have been employed in conjunction with the difficulty reducible oxide catalysts. In instances where these additives have been used it has been noted that they make the catalyst thermally less stable, thus reducing its life and increase the susceptibility of the catalyst to catalyst poisons.

[Price 1/-]

Price 3s. 6d.

The object of the present invention is to increase the activity of difficulty reducible oxide catalysts as dehydrogenation catalysts, particularly for the dehydrogenation of secondary aliphatic alcohols.

Another object is to improve the stability of dehydrogenation catalysts at high temperatures. Still another object is to make difficulty reducible oxide catalysts more resistant to catalyst poisons thus lengthening the active life of the catalysts. These and other objects will be apparent to those skilled in the art upon reading the following description.

It has been proposed in the past, to modify a dehydrating or dehydrogenating oxide catalyst by the addition thereto of a repressive agent, namely an oxide or compound more basic or acidic than the catalyst oxide according as the dehydrating or dehydrogenating effect is to be repressed. Bismuth oxide has itself been proposed as a dehydrogenation catalyst, and, as already mentioned, it has been proposed to add to a catalyst of this type alkali metal or alkaline earth oxides, hydroxides and carbonates in order to reduce undesirable dehydration side reactions. Acid oxides such as oxides of manganese, sulphur and phosphorus, tend to increase the dehydration activity at the expense of the dehydrogenation activity.

The present invention is based on the unexpected discovery that bismuth oxide itself when mixed with other difficulty reducible dehydrogenating metal oxides, the bismuth oxide being in the minor proportion, forms a dehydrogenation catalyst of outstanding good properties, the dehydration effect being reduced more effectively than by the addition of alkaline carbonates or similar conventional additives.

The present invention accordingly comprises a dehydrogenation catalyst comprising a major proportion of a difficulty reducible dehydrogenating metal oxide or mixtures of such oxides and a minor proportion of bismuth oxide (Bi_2O_3). It also includes in its scope a method of preparing such catalysts by mixing the powdered oxides together, forming a slurry by the addition of water, coating a

carrier with the slurry, followed by drying. In addition it includes the preferred use of these catalysts, namely the preparation of ketones from secondary aliphatic alcohols by passing the alcohol over the catalyst under conversion conditions of temperature and pressure.

As examples of suitable metal oxide catalysts with which the bismuth oxide may be mixed, may be mentioned the oxides of zinc, cerium and magnesium. The improvement obtained by using less than 1% of bismuth oxide is perceptible, but not sufficient to be of any material consequence, while the improvement engendered by the use of more than 6% of bismuth oxide is not sufficient over that obtained when using about 6% to warrant the additional expenditure.

Taking the preparation of $\text{ZnO}-\text{Bi}_2\text{O}_3$ catalyst as typical of the composition of this invention, it is preferred practice to mix the two oxides in the proper proportions in powdered form, then work in enough water to make a heavy slurry of the oxides, the slurry to be about the consistency of heavy cream. This will ordinarily require a volume of water approximately equivalent to the volume of powder used. The catalyst slurry is then coated on a carrier. This is conveniently accomplished by putting the catalyst support or carrier in a tumbling mechanism, pouring the catalyst slurry over the carrier and then tumbling until a uniform mix is secured. The mix is then placed in an oven at 80°C . and dried. The drying step generally requires from 24 to 48 hours. Pumice in granular or pill form or metal turnings such as those formed from copper or brass are the preferred carrier or catalyst support although other types of carriers are known to the art and perform equally well.

The catalysts of the present invention are extremely efficacious in the dehydrogenation of secondary alcohols such as isopropyl alcohol, secondary butyl alcohol, secondary amyl alcohol and homologues thereof to the corresponding ketones. The conversion of secondary alcohols to ketones is accomplished by passing the alcohol in vapor form through a catalyst packed tube heated to the temperature from 350° to 500°C . at a pressure of from about 1—3 atmospheres and a feed or feed rate of from 0.5 to 10 volumes of liquid alcohol per volume of catalyst per hour. The vapors are then passed to a condenser where the ketone and unreacted alcohol are condensed from the less readily condensable gases consisting predominantly of hydrogen and a small amount of, ordinarily not more than 1%, regenerated olefin.

Having outlined the general principles of the invention, the following examples which are included merely for purposes of illustration and not as a limitation, of the conversion of secondary butyl alcohol to methyl ethyl ketone run under the conditions indicated in each example graphically demonstrate the superiority of the present catalyst with respect to activity at high throughput, optimum temperature of reaction, thermal stability, longer life and resistance to poisons:—

CATALYST ACTIVITY

The increased activity of ZnO catalyst fortified with Bi_2O_3 is clearly demonstrated in example 1 below, which shows that $\text{ZnO}-\text{Bi}_2\text{O}_3$ at high feed rates maintains a conversion at a 90% level whereas ZnO alone and $\text{ZnO}+\text{Na}_2\text{CO}_3$ catalysts drop to 70%. Example 2 similarly shows the improved catalytic activity of $\text{ZnO}-\text{Bi}_2\text{O}_3$ catalyst with gradual increased feed rates.

EXAMPLE 1.

	Temp. 400°C . - 2 lbs./sq. in. gauge		
	Catalyst (on pumice)	ZnO	$\text{ZnO}+6\% \text{ Bi}_2\text{O}_3$
95	% conversion to ketone		
	@ 1.5 vol. alc/vol. cat/Hr.	93.0	92.0
	@ 6.0 vol. alc/vol. cat/Hr.	70.0	90.0

EXAMPLE 2.

	Temp. 400°C . - 2 lbs/sq. in. gauge		
	Catalyst (on brass)	$\text{ZnO}+6\% \text{ Na}_2\text{CO}_3$	$\text{ZnO}+6\% \text{ Bi}_2\text{O}_3$
100	% conversion to ketone		
	@ 1.5 v/v/Hr.	91.0	98.0
	@ 3.0	85.0	97.0
	@ 4.5	77.0	95.0
	@ 6.0	70.0	92.0

The increased activity of $\text{ZnO}-\text{Bi}_2\text{O}_3$ is further revealed in Example 3 below which shows that for a given conversion of alcohol to ketone the Bi_2O_3 fortified

catalyst permits a lower operating temperature. This holds true at normal and higher than normal feed rates.

EXAMPLE 3.

		Feed Rate 1.5 v/v/Hr. — 2 lbs./sq. in. gauge	
Catalyst (on brass)		ZnO + 6% Na ₂ CO ₃	ZnO + 6% Bi ₂ O ₃
5	% conversion to ketone		
	@ 350°C.	50.0	57.0
	@ 375°C.	68.0	90.0
19	@ 400°C.	91.0	98.0
	@ 350°C.	29.0	31.0
	@ 375°C.	43.0	62.0
		70.0	92.0

Feed Rate 6.0 v/v/Hr. — 2 lbs./sq. in. gauge

THERMAL STABILITY

EXAMPLE 4.

The ZnO-Bi₂O₃ catalyst can with-
stand extreme variations in temperature
without appreciably decreasing alcohol
conversion to ketone. The thermal
stability of a catalyst is closely related to
catalyst life and is important from a com-
mercial point of view in that temperature

fluctuations and shutdowns will not be of
serious consequence when a ZnO-Bi₂O₃
catalyst is employed.

In order to test the thermal stability of
the catalysts tests were run for a period of 25
5 hours each at 400°C., 500°C. and then
returned to 400°C. using a 1.5 v/v/Hr.
feed rate at 2 lbs./sq. in. gauge.

		ZnO	ZnO + 6% Na ₂ CO ₃	ZnO + 6% Bi ₂ O ₃
30	Catalyst (on brass)			
	% conversion to ketone			
	@ 400°C.	92.0	92.0	98.0
35	@ 500°C.	98.0	67.0	97.1
	@ 400°C.	78.0	53.0	90.0
35	Catalyst (on pumice)			
	% conversion to ketone			
	@ 400°C.	93.0	91.0	92.0
35	@ 500°C.	95.0	90.0	98.0
	@ 400°C.	64.0	72.0	82.0

CATALYST LIFE

The ZnO-Bi₂O₃ catalyst possesses a
longer active life than other conventional
catalysts. This is shown by an accelerated
life test, run simultaneously in the same
heating bath with the same alcohol feed.
This accelerated test was performed to
demonstrate, under adverse conditions for
the ZnO-Bi₂O₃, that a longer active life
is characteristic of the Bi₂O₃ fortified

catalyst. The ZnO-Na₂CO₃ catalyst at
increased feed rate converts only 70% of
the alcohol charged to ketone whereas
ZnO-Bi₂O₃ catalyst must maintain a
90% conversion. Any decrease in activity,
therefore, would be much more noticeable
with the ZnO-Bi₂O₃ catalyst. The results
are illustrated in Example 5 below, which
clearly shows the longevity of the
ZnO-Bi₂O₃ catalyst.

EXAMPLE 5.

		Temp. 400°C. — 2 lbs./sq. in. gauge — 6 v/v/Hr. Feed Rate	
		ZnO + 6% Na ₂ CO ₃	ZnO + 6% Bi ₂ O ₃
Days on Stream		% M.E.K.	% M.E.K.
60	4	70.0	92.0
	8	68.0	91.0
	12	68.0	91.0
65	16	68.0	91.0
	20	68.0	91.0
	24	66.0	91.0
70	28	61.0	91.0
	32	57.0	91.0
	36	51.0	89.0
75	40	43.0	86.0
	44	43.0	86.0
	48	34.0	88.0

75 RESISTANCE TO IMPURITIES IN FRESH STOCK

For a given alcohol quality a difficulty
reducible oxide dehydrogenation catalyst
containing Bi₂O₃ exhibits a marked
resistance to poisons. The secondary
butyl alcohol used for illustrative

purposes had the following composi-
tions.

92.4% Alcohol (by weight)
0.8% H₂O (by weight)
7.3% Impurities

85

100.0%

EXAMPLE 6.

Temp. 400°C. - 2 lbs./sq. in. gauge

Feed Rate = 1.5 v/v/Hr.

Catalyst % conversion to M.E.K.

ZnO + 6% Na ₂ CO ₃	86.0%
ZnO + 6% Bi ₂ O ₃	95.0%

Having now particularly described and ascertained the nature of the said invention, and in what manner the same is to be performed, as communicated to me by my foreign correspondents, I declare that what I claim is:—

1. A dehydrogenation catalyst comprising a major proportion of a difficultly reducible dehydrogenating metal oxide or mixtures of such oxides and a minor proportion of bismuth oxide (Bi₂O₃).

2. A catalyst according to Claim 1, wherein the metal oxide is an oxide of zinc, cerium or magnesium.

3. A catalyst according to Claim 1 or Claim 2, wherein the bismuth oxide is present in an amount of from 1% to 6% by weight based on the metal oxide or oxides.

4. A catalyst according to any of the preceding Claims, supported on a carrier such as pumice or metal turnings.

5. A dehydrogenation catalyst comprising a mixture of zinc oxide and 6% by weight of bismuth oxide based upon the zinc oxide supported on a carrier such as pumice or metal turnings.

6. A process for the preparation of a

catalyst according to Claim 4 or Claim 5, which comprises mixing the two oxides in powdered form, adding sufficient water to make a heavy slurry, coating the carrier with the slurry, and drying in an oven at 80°C.

7. A process for producing ketones which comprises passing a secondary aliphatic alcohol over a catalyst according to any of claims 1 to 5 under such temperature and pressure conditions as to effect the necessary conversion.

8. A process according to Claim 7, wherein the conditions are a temperature of from 350° C. to 500° C., and a pressure of from 1—3 atmospheres.

9. A process according to Claim 8, wherein the feed rate of the alcohol is from 0.5 to 10 volumes of liquid alcohol per volume of catalyst per hour.

10. A process according to any of Claims 7 to 9, wherein the alcohol is secondary butyl alcohol and the ketone is methyl ethyl ketone.

11. The processes for the preparation of methyl ethyl ketone, employing as a catalyst a mixture of zinc oxide and 6% by weight of bismuth oxide hereinbefore described with reference to examples 1 to 6.

Dated this 2nd day of August, 1945.

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